

PATENT SPECIFICATION

(11) 1 389 442

1 389 442

- (21) Application No. 5741/71 (22) Filed 2 March 1971
 (23) Complete Specification filed 2 June 1972
 (24) Complete Specification published 3 April 1975
 (51) INT CL² C07C 91/42, 89/00
 (52) Index at acceptance
 C2C 220 227 22Y 30Y 32Z 323 32Y 365 36Y 456 45Y 623
 630 660 662 680 682 699 793 797 79Y LG
 (72) Inventor PETER HOPE

(19)

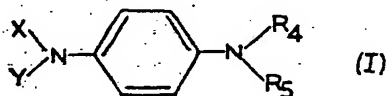


(54) NEW P-PHENYLENEDIAMINE DERIVATIVES AND USES THEREFOR

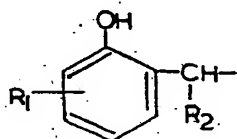
(71) We, KODAK LIMITED, a Company registered under the Law of England, of Kodak House, Station Road, Hemel Hempstead, Hertfordshire, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to certain *o*-hydroxybenzyl-*p*-phenylenediamine derivatives, and to their uses as anti-degradants in unsaturated elastomers and as modifiers in the vulcanization of elastomers.

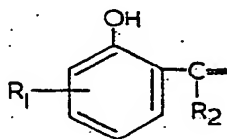
In accordance with the present invention, there is provided a compound of the formula:



wherein X is alkyl, cycloalkyl or hydrogen;
 Y is

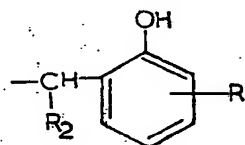


wherein R₁ is one or more of the following groups: alkyl, cycloalkyl, alkoxy, alkylthio, 3-hydroxy, 5-hydroxy, amino, 6-hydroxy, substituted amino, chloro or hydrogen; and R₂ is alkyl, cycloalkyl, aryl or hydrogen; or X and Y together are



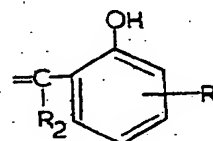
[Price 33p]

R₄ is alkyl, cycloalkyl or hydrogen
 R₅ is alkyl, aryl, hydrogen or



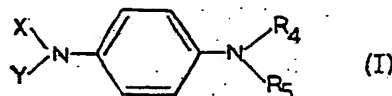
30

or R₄ and R₅ together are

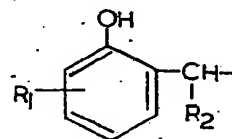


and in all cases where the compound contains more than one R₁ group, the R₁ groups may be the same or different, and where the compound contains more than one R₂ group, the R₂ groups may be the same or different.

Also in accordance with the present invention, there is provided a compound of the formula:



wherein X is alkyl, cycloalkyl or hydrogen;
 Y is



wherein R₁ is one or more of the following groups: alkyl, cycloalkyl, alkoxy, alkylthio, 3-hydroxy, 5-hydroxy, 6-hydroxy, amino, sub-

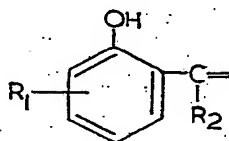
35

40

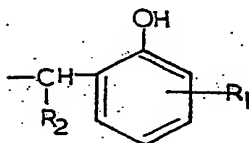
45

Am6

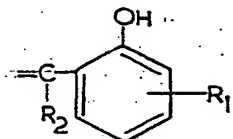
stituted amino, chloro or hydrogen; and R_2 is alkyl, cycloalkyl or hydrogen; or X and Y together are



- 5 R_1 is alkyl, cycloalkyl or hydrogen
 R_2 is alkyl, aryl, hydrogen or



or R_1 and R_2 together are



- 10 and in all cases where the compound contains more than one R_1 group, the R_1 groups may be the same or different, and where the compound contains more than one R_2 group, the R_2 groups may be the same or different.

- 15 In the above definitions, where alkyl, cycloalkyl and aryl groups are mentioned, it is to be understood that these terms include substituted alkyl, substituted cycloalkyl and substituted aryl groups.

- 20 Preferably the alkyl and cycloalkyl groups have from 1 to 15, especially 1 to 4, carbon atoms; more preferably the cycloalkyl groups have 5 or 6 carbon atoms. The preferred aryl group is phenyl. R_1 and R_2 may both represent an alkyl group having 1—4 carbon atoms or R_1 may be hydrogen and R_2 phenyl.

- 25 The present compounds may be prepared by the reaction of an appropriate *p*-phenylenediamine with an appropriate reactive *o*-hydroxybenzyl compound. Alternatively they may be prepared by reaction of an appropriate *p*-phenylenediamine with an appropriate aromatic ketone followed, if necessary, by reduction.

- 30 Compounds in accordance with the present invention have been found to be useful in protecting unsaturated elastomers, such as natural or synthetic rubber, from deterioration due to attack by air or ozone. Numerous compounds have been tried for this purpose but frequently have disadvantages in use, which may include an increase in the rate of cure of elastomeric articles in which they are compounded, and contact staining of adjoining

articles. Some known anti-degradants also tend to be rather easily leached out of the elastomer, for example by the action of rain water, leaving the article in an unprotected state.

Also in accordance with the present invention there is provided a method of curing a natural or synthetic unsaturated elastomer in which at least one compound of formula I (as defined in either of the above paragraphs) is added to a mix of the elastomer before curing thereof.

It is preferred to use an amount of the compound or compounds within the range of from 0.1 to 10 parts by weight per 100 parts by weight of the elastomer, more preferably within the range of from 0.5 to 5 parts by weight and still more preferably within the range of from 0.5 to 2.5 parts by weight per 100 parts by weight of the elastomer.

The invention also includes articles made from a mix of natural or synthetic unsaturated elastomer which has been cured in accordance with the method specified above.

It is found that compounds in accordance with the invention can advantageously modify the cure of unsaturated elastomers with which they are mixed. They tend to resist being leached out by aqueous solutions, e.g. rain water, from articles containing them, and cause less intense contact staining on adjacent articles than do many currently used anti-degradants. Natural or synthetic elastomers modified by compounding therewith at least one compound in accordance with the invention have good physical properties.

Methods in accordance with the present invention are particularly applicable to the vulcanization of elastomers cured by conventionally accelerated sulphur cure. It is possible to modify the effect of the conventional accelerator by the addition of a secondary accelerator and a retarder to the mix. Such modification can have advantageous effects on the cure, and can have practical and economic advantages in processing elastomers. Compounds in accordance with the present invention also have beneficial effects on curing when used as described above. The onset of vulcanisation is delayed but the actual rate of cross-linking of the elastomer is accelerated, and the overall cure time is about the same. It is possible for a single compound in accordance with the invention to replace three conventional additives used in curing and stabilization of elastomers, i.e. an anti-degradant, a secondary accelerator and a retarder.

The following Examples illustrate the present invention. All quantities are given in parts by weight.

Example 1.

3 - *t* - Butyl - 2 - hydroxy - 5 - methylbenzylpyridinium chloride (20.3g) and N,N-

5 dimethyl - *p* - phenylenediamine (9.5g) were refluxed in pyridine (85 ml) for 4 hours. On passing the pyridine solution into the water N - (3 - butyl - 2 - hydroxy - 5 - methyl - benzyl - N,N' - dimethyl - *p* - phenylenediamine (17.7g) crystallised.

milled and vulcanized by conventional procedures to 95% optimum cross-linked density and evaluated for physical properties. The compositions of the mixes are given in Table I and the physical properties in Table II below. Samples were evaluated both fresh and after ageing in air for seven days at 70°C.

Example 2.

Samples of five natural rubber mixes were

TABLE I

	Mix I	Mix II	Mix III	Mix IV	Mix V
Natural Rubber (Grade SMR 5)	100	100	100	100	100
Carbon Black (Grade HAF-LS)	50	50	50	50	50
Process Oil	3	3	3	3	3
Zinc Oxide	5	5	5	5	5
Stearic Acid	3	3	3	3	3
Accelerator (Cyclohexyl Benzthiazyl sulphenamide)	0.5	0.5	0.5	0.5	0.5
Sulphur	3	3	3	3	3
N-(α -phenyl-2-hydroxy-5-methyl benzyl)-N'-phenyl- <i>p</i> -phenylene diamine	—	2	—	—	2
N-(α -methyl-2-hydroxy-5-methyl benzyl)-N'-phenyl- <i>p</i> -phenylene diamine	—	—	2	—	—
N-(α -propyl-2-hydroxy-5-methyl benzyl)-N'-phenyl- <i>p</i> -phenylene diamine	—	—	—	2	—
N-(α -ethyl-2-hydroxy-5-methyl benzyl)-N'-phenyl- <i>p</i> -phenylene diamine	—	—	—	—	2

TABLE II

Properties of Fresh Sample	Mix I	Mix II	Mix III	MIX IV	Mix V
Monsanto Fatigue to failure - k/cycles	35.1	141.7	141.1	158.9	145.2
Dynamic Ozone Resistance - Hours to surface cracking at 25 pphm of ozone	<1	4	5	5	5
Static Ozone Resistance - Hours to surface cracking at 10% extension and 25 pphm of ozone	2	>100	>100	>100	74
Tensile strength - kgf/cm ²	258	268	282	269	275
Elongation at Break - %	470	480	500	470	500
After Air Ageing 7 days at 80°C					
Tensile Strength (% of original)	50	81	85	83	82
Elongation at Break (% of original)	60	71	70	72	75

Example 3.

Three natural rubber mixes were prepared and vulcanized by conventional procedures. The staining properties of an additive in accordance with the present invention (Mix VII) were compared with the staining proper-

ties of a conventional anti-degradant (Mix VIII) and with those of a control mix (Mix VI) containing no additive. The compositions of the mixes and the results of the staining tests are recorded below in Table III.

10

TABLE III

	Mix VI	Mix VII	Mix VIII
Natural Rubber	100	100	100
Carbon Black (Grade HAF)	50	50	50
Process Oil	3	3	3
Zinc Oxide	5	5	5
Stearic acid	2	2	2
Accelerator (cyclohexyl benzthiazyl sulphenamide)	0.5	0.5	0.5
Sulphur	3	3	3
N-(3-t-butyl-2-hydroxy- 5-methylbenzyl)-N',N'- dimethyl-p-phenylene diamine)	—	2	—
N-isopropyl-N'-phenyl- p-phenylene diamine	—	—	2
Contact staining of cellulose plate	None	Medium dark	very dark

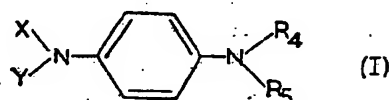
Example 4.

Five further rubber mixes were prepared, three of these containing respectively 0.5, 1.0 and 2.5 parts by weight per hundred parts of rubber of N - (3 - t - butyl - 2 - hydroxy-5 - methylbenzyl) - N,N' - dimethyl - p-phenylenediamine. The fourth sample contained 2 parts by weight per hundred parts of rubber of N - isopropyl - N' - phenyl - p-phenylenediamine, and the fifth sample contained neither of these additives. These further samples were milled and cured by the conventional procedures. In each case, the progress of curing was followed on a rheometer, and the resulting curves are shown on the drawing accompanying the Provisional Specification, which is a graph of torque inch pounds against time.

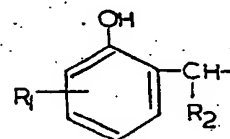
It will be seen from the graph that the curves for the control mix containing neither additive and for the comparative mix containing n - isopropyl - N' - phenyl - p-phenylenediamine are not very different. The three curves for the three mixes containing the compound in accordance with the invention were so similar that they are shown as a single curve, and they indicate that the compound delayed the onset of cure, and accelerated the actual cure, finishing with a higher degree of cure.

WHAT WE CLAIM IS:—

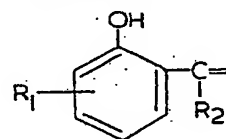
1. A compound of the formula:



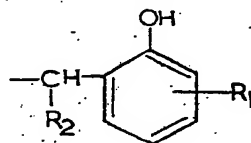
wherein X is alkyl, cycloalkyl or hydrogen; Y is



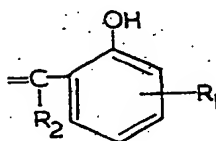
wherein R₁ is one or more of the following groups: alkyl, cycloalkyl, alkoxy, alkylthio, 3-hydroxy, 5-hydroxy, 6-hydroxy, amino, substituted amino, chloro or hydrogen; and R₂ is alkyl, cycloalkyl, aryl or hydrogen; or X and Y together are



R_4 is alkyl, cycloalkyl or hydrogen;
 R_5 is alkyl, aryl, hydrogen or



or R_4 and R_5 together are



5

and in all cases where the compound contains more than one R_1 group, the R_1 groups may be the same or different, and where the compound contains more than one R_2 group, the R_2 groups may be the same or different.

2. A compound as claimed in Claim 1 in which R_2 is an alkyl group of 1—15 carbon atoms or a phenyl group.

3. A compound as claimed in Claim 1 or 2 in which R_1 is an alkyl group of 1—15 carbon atoms.

4. A compound as claimed in any of Claims 1—3 in which R_4 and R_5 are both alkyl groups having 1—4 carbon atoms or R_4 is hydrogen and R_5 is phenyl.

5. A compound according to Claim 1 substantially as hereinbefore described and with reference to the Examples.

6. A method of curing a natural or synthetic unsaturated elastomer in which at least one compound of formula I according to Claim 1 is added to a mix of the elastomer before curing thereof.

7. A method as claimed in Claim 6 in which the compound of Formula I is used in an amount of from 0.1 to 10 parts by weight per 100 parts by weight of the elastomer.

8. A method as claimed in Claim 6 in which the compound of Formula I is used in an amount of from 0.5 to 5.0 parts by weight per 100 parts by weight of the elastomer.

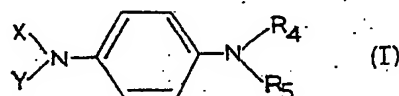
9. A method as claimed in Claim 6 in which the compound of Formula I is used in an amount of from 0.5 to 2.5 parts by weight per 100 parts by weight of the elastomer.

10. A method according to any of Claims 6 to 9 in which the elastomer is natural rubber.

11. A method according to Claim 6 substantially as hereinbefore described and with reference to the Examples.

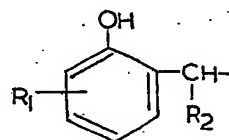
12. Articles made from a mix of natural or synthetic unsaturated elastomer which has been cured by the method of any of Claims 6—11.

13. A compound of the formula:



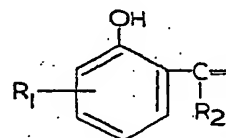
wherein X is alkyl, cycloalkyl or hydrogen;

Y is



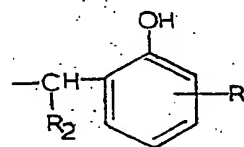
55

wherein R_1 is one or more of the following groups: alkyl, cycloalkyl, alkoxy, alkylthio, 3-hydroxy, 5-hydroxy, 6-hydroxy, amino, substituted amino, chloro or hydrogen; and R_2 is alkyl, cycloalkyl or hydrogen; or X and Y together are



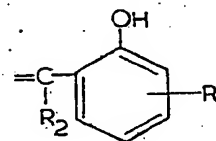
R_4 is alkyl, cycloalkyl or hydrogen
 R_5 is alkyl, aryl, hydrogen or

60



65

or R_4 and R_5 together are



and in all cases where the compound contains more than one R_1 group, the R_1 groups may be the same or different, and where the compound contains more than one R_2 group, the R_2 groups may be the same or different.

70

14. A compound as claimed in Claim 13 in which R_2 is an alkyl group of 1—15 carbon atoms.

15. A method of curing a natural or synthetic unsaturated elastomer in which at least one compound of formula I according to

75

Claim 13 is added to a mix of the elastomer before curing thereof.

5 16. A method as claimed in Claim 15 in which the compound of Formula I is used in an amount of from 0.1 to 10 parts by weight per 100 parts by weight of the elastomer.

10 17. A method as claimed in Claim 15 in which the compound of Formula I is used in an amount of from 0.5 to 5.0 parts by weight per 100 parts by weight of the elastomer.

18. A method as claimed in Claim 15 in which the compound of Formula I is used in an amount of from 0.5 to 2.5 parts by

weight per 100 parts by weight of the elastomer. 15

19. A method according to any of Claims 15 to 18 in which the elastomer is natural rubber.

20. Articles made from a mix of natural or synthetic unsaturated elastomer which has been cured by the method of any of Claims 15 to 19. 20

L. A. TRANGMAR,
BSc., CPA,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

